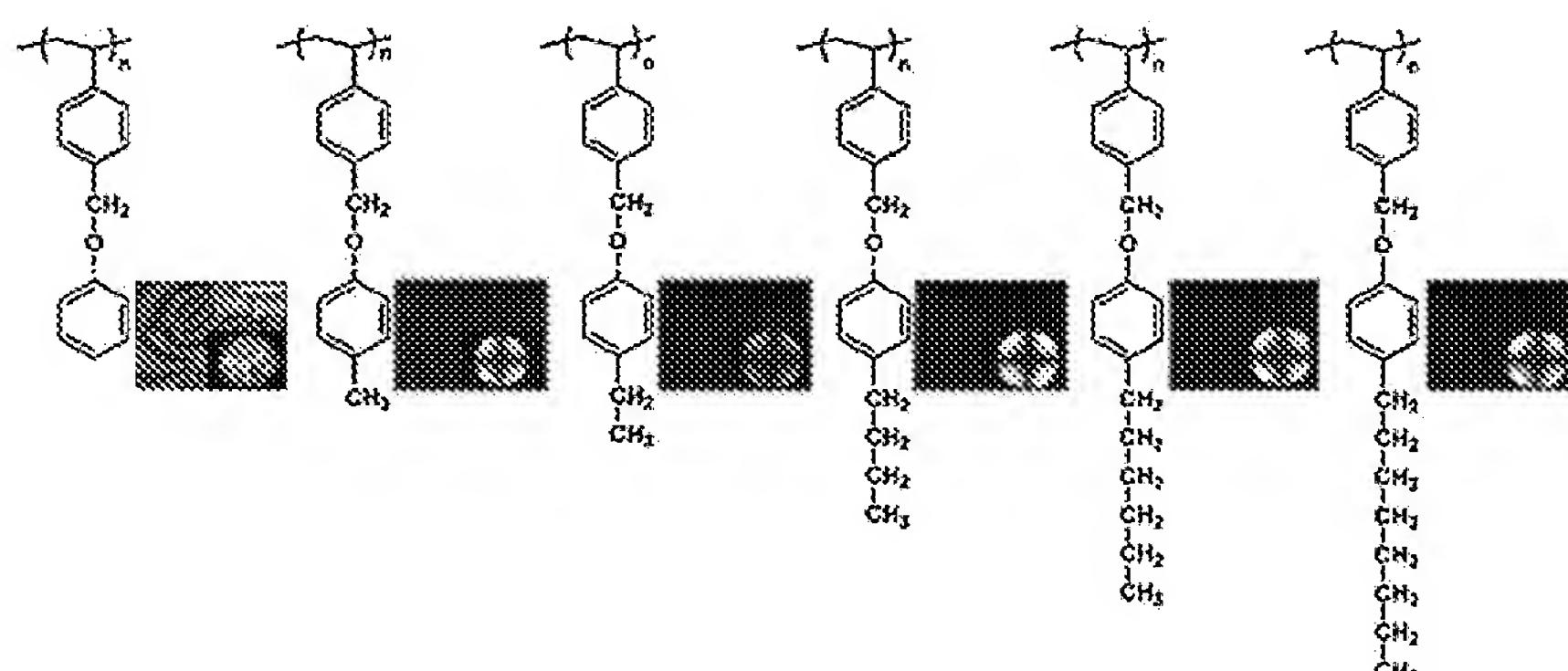


EXHIBIT C

4-Alkylphenoxyethyl-Substituted Polystyrenes for Liquid Crystal Alignment Layers^a

Hyo Kang, Tae-Ho Kim, Daeseung Kang, Jong-Chan Lee*

We synthesized a phenoxyethyl-substituted polystyrene (PHP) and a series of 4-alkylphenoxyethyl-substituted polystyrenes, where the alkyl group is $-(CH_2)_nH$ ($n = 1, 2, 4, 6$, and 8), using polymer analogous reactions, in order to study the effect of the phenoxyethyl and 4-alkylphenoxyethyl side groups on the liquid crystal (LC) alignment properties. The LC cell fabricated with the rubbed PHP film exhibited homogeneous planar and perpendicular LC alignment with respect to the rubbing direction. On the contrary, the LC cells made from the 4-alkylphenoxyethyl-substituted polystyrenes showed homeotropic LC alignment behaviors even at a very high rubbing density of 250 , regardless of the length of the alkyl groups. Previously, n -alkylsulfonylmethyl-substituted polystyrenes with alkyl groups having more than 8 carbons ($n > 8$) showed homeotropic LC alignment behavior. Therefore, the additional phenoxy group in the side chain was found to improve the homeotropic LC aligning ability of the polystyrene derivatives.



Introduction

Liquid crystal (LC) alignment has been intensively studied due to the scientific and technical interest in the liquid crystal display (LCD) industry.^[1] Polyimide (PI) derivatives have been most widely used as the LC alignment layers for producing homogeneous planar or homeotropic LC alignment of LC cells,^[2] while other alignment methods based on nanotechnologies using nanostructures such as polyhedral oligomeric silsesquioxane, carbon-based nanomaterials, and others have been recently developed to control anchoring conditions of LC molecules on surfaces.^[3] Homeotropic LC alignment methods have some advantages over homogeneous planar LC alignment ones, because the

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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mcp-journal.de>, or from the author.

LC cells fabricated using the homeotropic LC alignment methods have better electro-optical performance, such as a faster response time and higher contrast ratio.^[4] PI derivatives having long alkyl or alkyloxy groups, such as semi-flexible copolyimides containing *n*-octadecyl side groups and PIs with (*n*-decyloxy)biphenyloxy side groups, show homeotropic LC alignment behavior.^[5-8] Polystyrene (PS) derivatives having long alkyl chains can also produce homeotropic LC alignment layers. For example, LC cells fabricated using a nematic LC (ZLI-5900-000, Merck Co.) and rubbed polymer films of *n*-alkylsulfonylmethyl- and *n*-alkylthiomethyl-substituted polystyrenes having more than eight carbons (*n* > 8) show homeotropic LC alignment behavior.^[9]

In this study, we found that LC cells fabricated using 4-alkylphenoxyethyl-substituted polystyrenes having short alkyl chains show homeotropic LC alignment behavior. The synthesis and characterization of these polymers and the optical properties of the LC cells fabricated using the unrubbed or rubbed polymer films are also included.

Experimental Part

Materials

Styrene, 4-chloromethylstyrene, 4-methylphenol, 4-ethylphenol, and 4-octylphenol were purchased from Aldrich Chemical Co., nematic LC (5CB) was purchased from Merck Co., and 4-butylphenol and 4-hexylphenol were purchased from TCI. These chemicals were used as received. *N,N'*-Dimethylacetamide (DMAc, Aldrich) was dried over molecular sieves (4 Å). Tetrahydrofuran (THF, Aldrich) was dried by refluxing with benzophenone and sodium followed by distillation. 4-Chloromethylstyrene (Aldrich) was purified by column chromatography on silica gel using hexane as an eluent to remove any impurities and inhibitors (*tert*-butylcatechol and nitroparaffin). 2,2'-Azobisisobutyronitrile (AIBN, Junsei Chemical Co. Ltd.) was used as an initiator. AIBN was purified from recrystallization using methanol. Poly(chloromethylstyrene) (PCMS of $\overline{M}_n = 18\,500$, $\overline{M}_w/\overline{M}_n = 2.40$, and $T_g = 106^\circ\text{C}$) and polystyrene (PS of $\overline{M}_n = 37\,000$, $\overline{M}_w/\overline{M}_n = 2.02$, and $T_g = 104^\circ\text{C}$) were obtained through conventional free radical polymerization of 4-chloromethylstyrene (8.0 g, 52.6 mmol) and styrene (2.0 g, 1.92 mmol), respectively, using AIBN (2.0 wt.-% based on monomer) in dried THF (20 mL) under nitrogen atmosphere.^[10] All other reagents and solvents were used as received.

Preparation of Phenoxyethyl-Substituted Polystyrene (PHP) and 4-Alkylphenoxyethyl-Substituted Polystyrenes

The following procedure was used to synthesize all the 4-alkylphenoxyethyl-substituted polystyrenes, where the alkyl group is $-(\text{CH}_2)_n\text{H}$ ($n = 1, 2, 4, 6$, and 8). The synthesis of 4-ethylphenoxyethyl-substituted polystyrene (P4EP) is given

as an example. A mixture of 4-ethylphenol (0.430 g, 3.55 mmol, 180 mol-% compared with PCMS) and potassium carbonate (0.545 g, 3.94 mmol, 200 mol-% compared with PCMS) in *N,N'*-dimethylacetamide (DMAc, 10 mL) was heated to 80°C . PCMS (0.3 g, 1.97 mmol) solution in DMAc (10 mL) was added to the mixture and then magnetically stirred at 80°C for 12 h under nitrogen atmosphere. The solution mixture was cooled to room temperature and then poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitation times from DMAc solution into methanol and then washed with water to remove any potassium carbonate and remaining salts. The product was obtained in above 80% yield after dried under a vacuum overnight. This polymer was designated as P4EP.

P4EP ^1H NMR (CDCl₃): 1.0–1.2 (t, 3H, $-\text{O}-\text{Ph}-\text{CH}_2-\text{CH}_3$), 1.2–1.5 (m, 2H, $-\text{CH}_2-\text{CH}-\text{Ph}-$), 1.6–2.1 (m, 1H, $-\text{CH}_2-\text{CH}-\text{Ph}-$), 2.4–2.7 (m, 2H, $-\text{Ph}-\text{CH}_2-\text{CH}_3$), 4.6–5.0 (s, 2H, $-\text{Ph}-\text{CH}_2-\text{O}-$), 6.2–6.7 (m, 2H, $-\text{O}-\text{PhH}-\text{CH}_2-\text{CH}_3$), 6.7–6.9 (m, 2H, $-\text{O}-\text{PhH}-\text{CH}_2-\text{CH}_3$), 6.9–7.2 (m, 4H, $-\text{CH}-\text{PhH}-\text{CH}_2-\text{O}-$).

P4EP IR (KBr): 2 923 (asymmetric aliphatic C–H stretching), 2 856 (symmetric aliphatic C–H stretching), 1 607 (ring C=C stretching), 1 508 (ring C=C stretching of the phenoxy unit).

The degree of substitution was calculated by comparing the multiplet at 2.4–2.7 ppm (2H) with the backbone peak at 1.2–2.1 ppm (3H) which included the contribution of residual PCMS and found to be almost 100% within experimental error. PHP, 4-methylphenoxyethyl-substituted polystyrene (P4MP), 4-butylphenoxyethyl-substituted polystyrene (P4BP), 4-hexylphenoxyethyl-substituted polystyrene (P4HP), and 4-octylphenoxyethyl-substituted polystyrene (P4OP) were synthesized from the same procedure, except that phenol, 4-methylphenol, 4-butylphenol, 4-hexylphenol, and 4-octylphenol, respectively, were used instead of 4-ethylphenol. ^1H NMR data of these polymers are shown in Table 1.

The copolymers of P4EP, designated as P4EP_x, where x is the degree (%) of substitution of chloromethyl to 4-ethylphenoxyethyl group, were prepared from the same procedure, which was used for P4EP, except that less than 180 mol-% of 4-ethylphenol was used. For example, P4EP78, P4EP60, P4EP37, and P4EP20 were prepared with 4-ethylphenol of 0.192 g (1.58 mmol), 0.144 g (1.18 mmol), 0.096 g (0.79 mmol), and 0.048 g (0.39 mmol), respectively, using slight excess amounts of potassium carbonate (0.545 g, 3.94 mmol, 200 mol-% compared with PCMS).

Film Preparation and LC Alignment Process

Solutions of the polymers in toluene (2 wt.-%) were filtered using a PTFE membrane with a pore size of 0.45 μm . Thin films of the polymers were prepared by spin-coating (2 000 rpm, 30 s) onto 1.5 × 1.5 cm² indium tin oxide (ITO) coated glass and 1.5 × 2.0 cm² polyethylene terephthalate (PET) substrates. The polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp.). The rubbing density equation is written as $L/l = N[(2\pi rn/60v) - 1]$, where L is the total length of the rubbing cloth (mm), l the contact length of the circumference of the rubbing roller (mm), N the cumulative number of rubbings, n the speed (rpm) of the rubbing roller, r the radius (cm) of rubbing roller, and v the velocity (cm · s⁻¹) of the substrate stage.^[2;2k]

Table 1. ^1H NMR characterization of the polymers.

Polymer	Chemical shifts (δ , ppm) and assignments
PHP	$\delta = 1.0\text{--}1.5$ (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.3 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 4.7–5.1 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.2–6.8 (m, 2H, $-\text{CH}_2\text{--O--PhH}$), 6.8–7.0 (m, 3H, $-\text{CH}_2\text{--O--PhH}$), 7.0–7.2 (m, 2H, $-\text{CH--PhH--CH}_2\text{--O--}$), 7.2–7.4 (m, 2H, $-\text{CH--PhH--CH}_2\text{--O--}$)
P4MP	$\delta = 1.0\text{--}1.5$ (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.1 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 2.1–2.4 (s, 3H, $-\text{O--Ph--CH}_3$), 4.6–5.1 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.1–6.6 (m, 2H, $-\text{O--PhH--CH}_3$), 6.6–6.9 (m, 2H, $-\text{O--PhH--CH}_3$), 6.9–7.2 (m, 4H, $-\text{CH--PhH--CH}_2\text{--O--}$)
P4EP	$\delta = 1.0\text{--}1.2$ (t, 3H, $-\text{O--Ph--CH}_2\text{--CH}_3$), 1.2–1.5 (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.1 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 2.4–2.7 (m, 2H, $-\text{Ph--CH}_2\text{--CH}_3$), 4.6–5.0 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.2–6.7 (m, 2H, $-\text{O--PhH--CH}_2\text{--CH}_3$), 6.7–6.9 (m, 2H, $-\text{O--PhH--CH}_2\text{--CH}_3$), 6.9–7.2 (m, 4H, $-\text{CH--PhH--CH}_2\text{--O--}$)
P4BP	$\delta = 0.8\text{--}1.0$ [t, 3H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_2\text{--CH}_3$], 1.1–1.4 [m, 4H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_2\text{--CH}_3$], 1.4–1.6 (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.1 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 2.4–2.6 [m, 2H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_2\text{--CH}_3$], 4.6–5.1 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.2–6.7 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_4\text{--H}$], 6.7–6.9 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_4\text{--H}$], 6.9–7.2 (m, 4H, $-\text{CH--PhH--CH}_2\text{--O--}$)
P4HP	$\delta = 0.8\text{--}1.0$ [t, 3H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_4\text{--CH}_3$], 1.1–1.4 [m, 8H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_4\text{--CH}_3$], 1.4–1.6 (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.1 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 2.4–2.6 [m, 2H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_4\text{--CH}_3$], 4.6–5.0 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.2–6.7 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_6\text{--H}$], 6.7–6.9 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_6\text{--H}$], 6.9–7.2 (m, 4H, $-\text{CH--PhH--CH}_2\text{--O--}$)
P4OP	$\delta = 0.8\text{--}1.0$ [t, 3H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_6\text{--CH}_3$], 1.1–1.4 [m, 12H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_6\text{--CH}_3$], 1.4–1.6 (m, 2H, $-\text{CH}_2\text{--CH--Ph--}$), 1.6–2.1 (m, 1H, $-\text{CH}_2\text{--CH--Ph--}$), 2.4–2.6 [m, 2H, $-\text{Ph--CH}_2\text{--}(\text{CH}_2)_6\text{--CH}_3$], 4.6–5.1 (s, 2H, $-\text{Ph--CH}_2\text{--O--}$), 6.2–6.7 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_8\text{--H}$], 6.7–6.9 [m, 2H, $-\text{O--PhH--}(\text{CH}_2)_8\text{--H}$], 6.9–7.2 (m, 4H, $-\text{CH--PhH--CH}_2\text{--O--}$)

LC Cell Assembly

Antiparallel LC cells were fabricated using the unrubbed or rubbed polymer films onto ITO coated glass slides and PET substrates. The antiparallel LC cells were constructed by assembling the polymer films together antiparallel with respect to the rubbing direction using spacers with thicknesses of 6.5 and 50 μm . The fabricated LC cells were filled with a nematic LC, 5CB (Merck Co., 4-cyano-4'-pentylbiphenyl, $n_e = 1.736$, $n_o = 1.5442$, and $\Delta\epsilon = 14.5$, where n_e , n_o , and $\Delta\epsilon$ represent extraordinary refractive indexes, ordinary refractive indexes, and dielectric anisotropy, respectively), in isotropic state in order to avoid creating flow alignment by the capillary action. The manufactured LC cells were sealed with epoxy.

Instrumentation

^1H NMR measurements were carried out on a Bruker AVANCE at 300 MHz. FT-IR spectra were recorded 4 cm^{-1} resolution and interferograms were accumulated 64 times. Gel permeation chromatography (GPC) was used to measure the number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of synthesized polymer with respect to polystyrene standards using THF as an eluent and a UV detector. Differential scanning calorimeter (DSC) measurements were carried out on TA instruments 2920 at a heating and cooling rate of 20 $^\circ\text{C}\cdot\text{min}^{-1}$.

under a nitrogen atmosphere. Thermal gravimetric analysis (TGA-2050, TA instrument) was used to investigate thermal stability of polymers. Polymer samples were heated from room temperature to 800 $^\circ\text{C}$ at the heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. The contact angles of distilled water and methylene iodide on polymer films were determined with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The Owens-Wendt's equation was applied to calculate the surface energy values from the static contact angles.^[11] The topography of the unrubbed and rubbed polymer films in an area of $3 \times 3 \mu\text{m}^2$ was examined using atomic force microscopy (AFM, XE-150, PSIA) in noncontact mode (spring constant of the cantilever: 0.6 $\text{N}\cdot\text{m}^{-1}$, scan rate: 1 Hz). For transmission electron microscopy (TEM) measurement, the 2 wt-% solution of polymers in toluene was dropped onto carbon-coated copper grid. Just after vacuum evaporation of the solvent, thin polymer films formed between copper grid lines were observed from the transmittance for 120 keV using TEM (LIBRA 120, Carl Zeiss, Inc.). The LC alignment direction of the antiparallel LC cells was investigated by measuring the angular dependence of absorbance of a dichroic dye (disperse blue 1, Aldrich), which was dissolved in 5CB at a concentration of 1 wt-%, using optical apparatus equipped with a He-Ne laser, a polarizer, and a photodiode detector as a function of rotation angle of samples.^[12] The pretilt angle of LCs of antiparallel LC cell was measured by the crystal rotation method.^[12] The cell gap was measured before filling the LCs using a spectrophotometer (Ocean

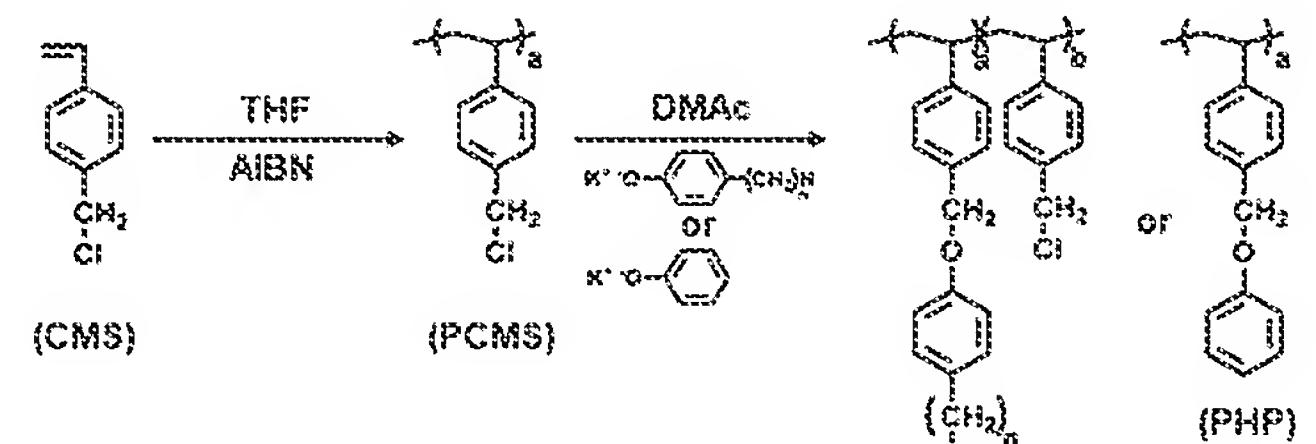


Optics, Inc., S 2000). The polarized optical microscopy (POM) images of LC cell were observed from an optical microscopy (Nikon, ECLIPSE E600 POL) equipped with a polarizer and digital camera (Nikon, COOLPIX995).

Results and Discussion

Figure 1 shows the synthetic routes to the PHP and 4-alkylphenoxyethyl-substituted polystyrenes (P4MP, P4EP, P4BP, P4HP, and P4OP). The copolymers of P4EP with different degrees (%) of substitution were obtained by varying the amounts of 4-ethylphenol in the reaction. Almost 100% conversions from chloromethyl to 4-alkylphenoxyethyl were obtained, when 180 mol-% of 4-alkylphenol was used at 80 °C for 12 h. The average molecular weights (\bar{M}_n) of the polymers modified from the PCMS ($\bar{M}_n = 18\,500$) were always larger than 20\,500 (Table 2), indicating that the polymer modification from PCMS to the products gave rise to an increase in the average molecular weights of the polymers, as expected. These polymers are soluble in many medium-polarity solvents having low boiling points, such as THF and chloroform, and in aprotic polar solvents, such as DMF, NMP, and DMAc.

The FT-IR spectra of the polymers were measured and the peaks were characterized with the aid of the previously reported results for other polymers (Figure 2).^[13] The peaks of the characteristic band of the stretching vibrational mode of chloromethyl in PCMS at 661 cm^{-1} completely disappeared, indicating that the chloromethyl group was changed to phenoxyethyl or 4-alkylphenoxyethyl groups through the polymer analogous reactions.



(P4MP (n=1), P4EPx (n=2),
P4BP (n=4), P4HP (n=6),
and P4OP (n=8))

Where x is the degree (%) of substitution.

Figure 1. Synthetic routes to the 4-alkylphenoxyethyl-substituted polystyrenes, where the alkyl group is $-(\text{CH}_2)_n\text{H}$ ($n = 1, 2, 4, 6$, and 8).

The thermal properties of the polymers were investigated using DSC and TGA. All of the polymers were found to be amorphous, since only glass transitions were observed in their DSC thermograms (Figure 3 and Table 2). As the number of carbon atoms in the alkyl part of the 4-alkylphenoxy side group increases from 0 to 8, the T_g value decreases from 71 °C for PHP to 11 °C for P4OP. The decrease of the T_g value of the polystyrene derivatives with increasing length of the alkyl side groups was reported before and was ascribed to the increase of the free volume in the polymer, because polymers having larger free volumes have lower T_g values.^[9,14] In the case of the polystyrene derivatives in this study, we believe that the incorporation of the 4-alkylphenoxyethyl groups onto the phenyl side groups of the polystyrene increases the free volume and that this lowers the T_g s of the polymers. The thermal decomposition behavior of the polymers was also found to

Table 2. Results of the characterization of the polymers using $^1\text{H-NMR}$, GPC, DSC, and TGA.

Polymer designation	Degree of substitution %	\bar{M}_n ^{a)}	\bar{M}_w/\bar{M}_n ^{a)}	T_g °C	$T_{d,90\%}$ ^{b)} °C	Char yield ^{c)} °C
PS		37\,000	2.02	104	363	0.2
PHP	≈100	21\,700	2.25	71	342	14.6
P4MP	≈100	22\,600	3.00	67	352	21.0
P4EP	≈100	22\,900	3.08	48	350	16.7
P4EP78	78	21\,900	2.97	63	339	17.9
P4EP60	60	21\,500	2.70	69	337	19.6
P4EP37	37	20\,900	3.10	82	334	22.7
P4EP20	20	20\,500	3.17	83	328	24.5
P4BP	≈100	23\,300	3.02	38	342	12.1
P4HP	≈100	25\,800	2.82	21	331	11.7
P4OP	≈100	26\,500	2.95	11	299	8.2

^{a)}Obtained from GPC using THF as solvent with respect to monodisperse polystyrene as standards; ^{b)}the decomposition temperature ($T_{d,90\%}$) is defined as 10 wt.-% loss; ^{c)}the Char yield at 800 °C.

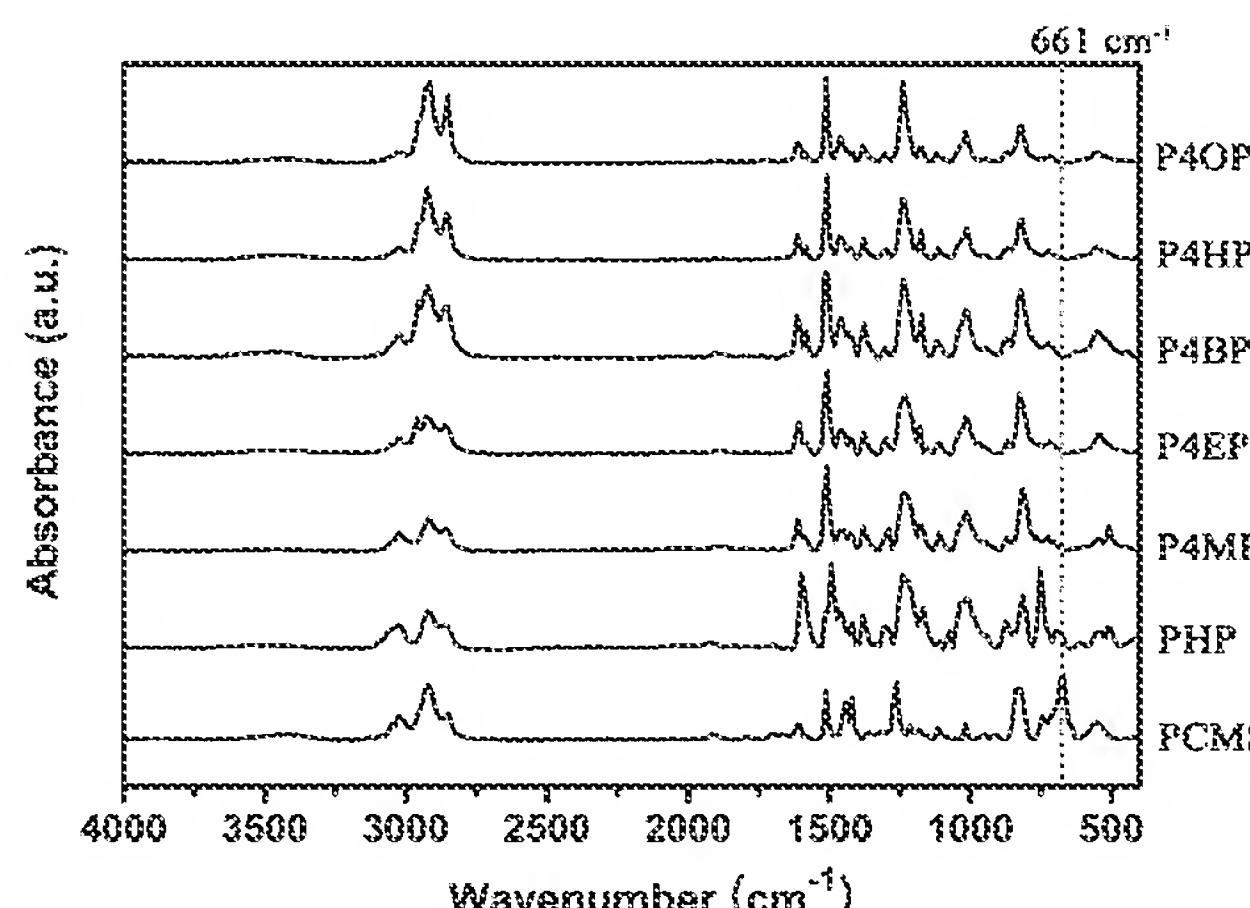


Figure 2. FT-IR of the polymers.

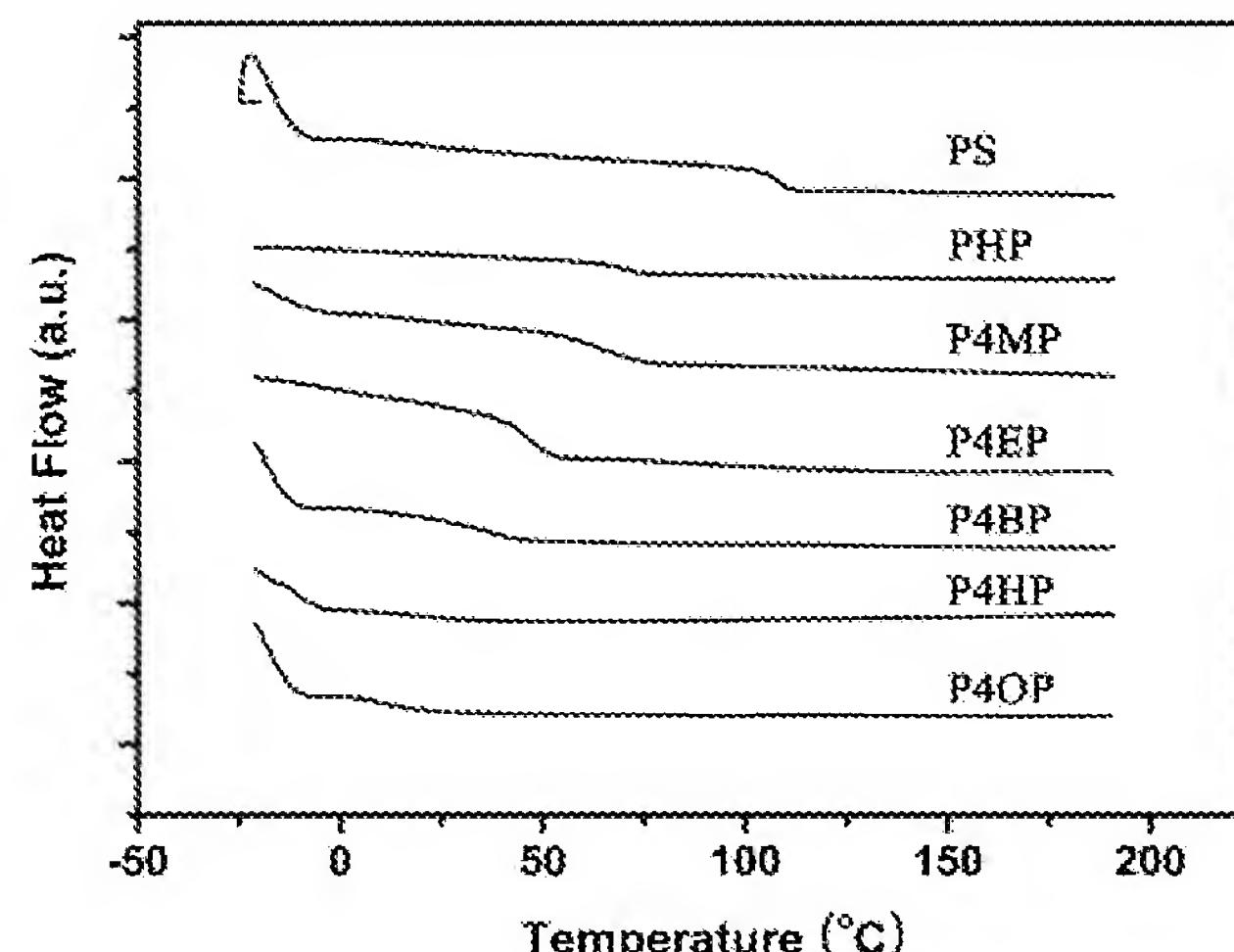


Figure 3. DSC thermograms of the polymers.

be affected by the number of carbon atoms in the 4-alkylphenoxy side groups. As the number of carbon atoms in the 4-alkylphenoxy side groups increases, the decomposition temperature ($T_{d,90\%}$) of the polymers decreases from 352 °C for P4MP to 299 °C for P4OP and the char yield (%) of the polymers at 800 °C decreases from 21.0% for P4MP to

8.2% for P4OP (Table 2). Conclusively, as the number of alkyl groups in the 4-alkylphenoxy side groups increases, the T_g , $T_{d,90\%}$, and char yield of the polymers decrease.

The LC alignment behavior of the LC cells made from the unrubbed polymers and 5CB was determined by observing the POM images, as shown in Figure 4. Random planar LC

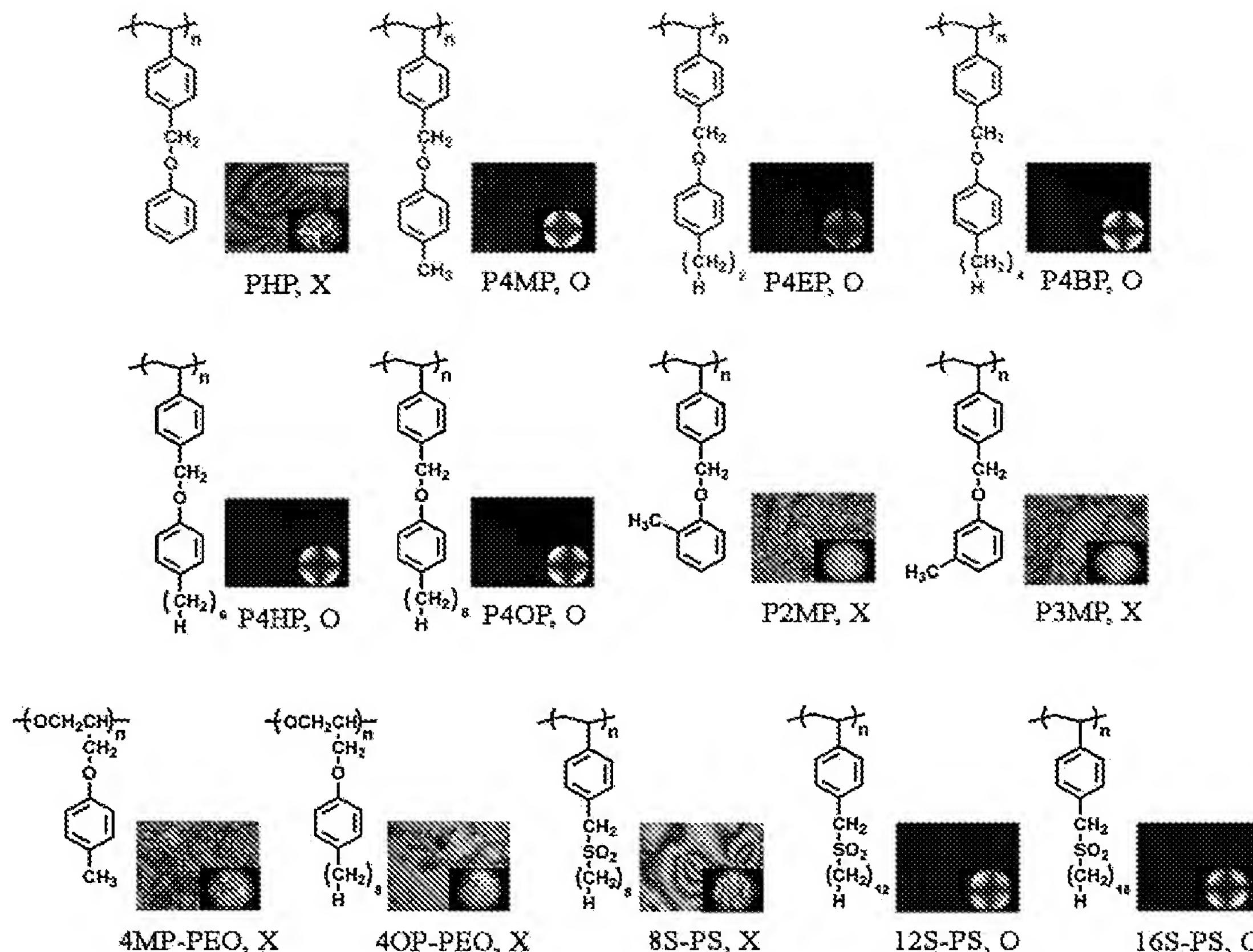


Figure 4. Structures and POM images for the LC cells made from polymer films for homeotropic LC alignment studies. These polymers were synthesized using the similar procedure as those for P4EP and the degrees of the substitution were over 95%. Circle (○) and cross (×) indicate unrubbed polymer film have homeotropic and poor LC aligning ability, respectively.

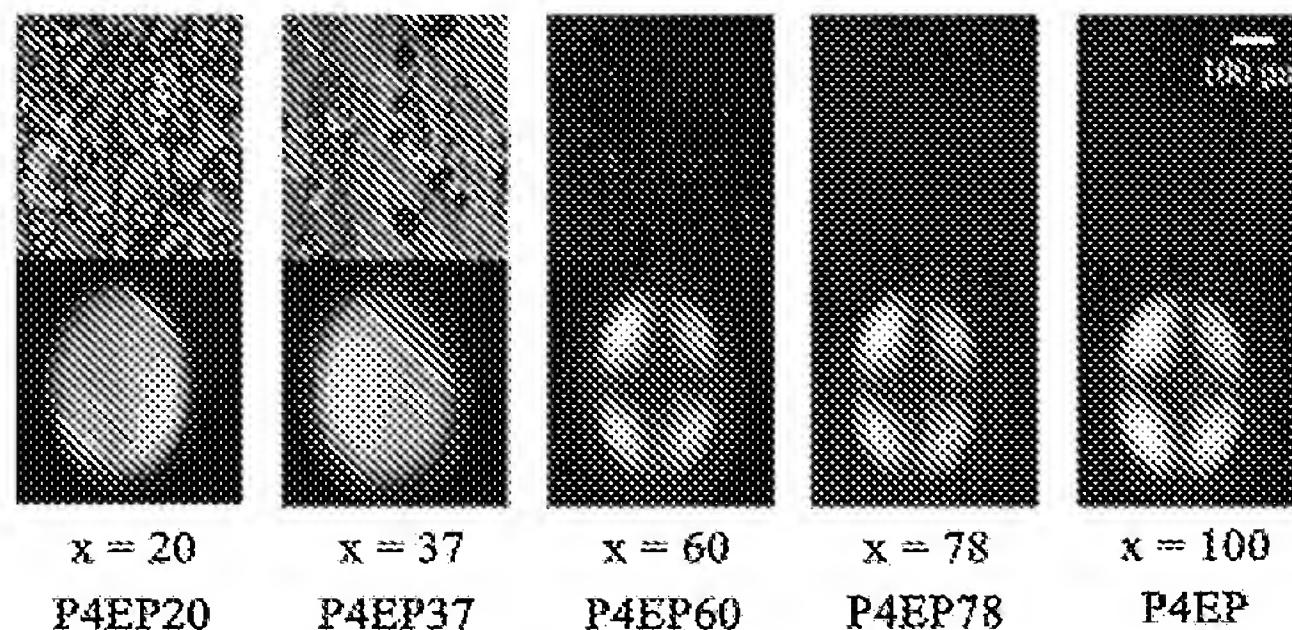


Figure 5. Orthoscopic and conoscopic POM images of the LC cells made from unrubbed P4EP_x films on the molar content of the 4-ethylphenoxyethyl side groups [x = the molar content (%) of 4-ethylphenoxyethyl moiety].

alignment was observed for the LC cells made from the unrubbed PS (image not shown) and PHP films, while all of the LC cells made from the unrubbed 4-alkylphenoxy-methyl-substituted polystyrene (P4MP, P4EP, P4BP, P4HP, and P4OP) films showed homeotropic LC alignment behavior. We also tried to investigate the effect of the amount of 4-alkylphenoxyethyl moieties in the side chain on the homeotropic LC alignment properties. Figure 5 shows the orthoscopic and conoscopic POM images of the LC cells made from the unrubbed films of the P4EP copolymers and 5CB. Homeotropic LC alignment behavior was observed over the whole area when the molar content of the 4-ethylphenoxyethyl containing monomeric unit in the P4EP_x was larger than about 60%.

The LC alignment direction was investigated by observing the polar diagrams of the absorbance of a dichroic dye (disperse blue 1) in the anti-parallel LC cells fabricated using 5CB and the rubbed polymer films with a rubbing density of 100. The LC cell made from the rubbed PHP film shows a maximum absorbance along the $90 \rightarrow 270^\circ$ direction, which is perpendicular with respect to the rubbing direction [Figure 6(a)]. It has been known that the rubbed surface of PS film can induce homogeneous planar and perpendicular LC alignment with respect to the rubbing direction^[15] and we also found that this occurred

in the LC cells fabricated using the rubbed PS films with a rubbing density of 100. However, the homogeneity of the LC cells fabricated with the rubbed PHP and PS films with a rubbing density of 100 was lost after several days as previously described in other research group,^[15] indicating that the rubbed surface of PHP and PS cannot produce reliable LC alignment layers. We found that the micro-groove structure of the films generated from the rubbing process remains after 7 d from AFM study shown in the Supporting Information. Therefore, the loss of the homogeneity should not be caused by the changes of the morphological microstructures but arisen by the changes in the molecular level. Further detailed studies are needed to verify this, while they are beyond the scope of this paper. On the contrary, all of the rubbed and unrubbed films of the 4-alkylphenoxyethyl-substituted polystyrenes were able to produce stable homeotropic LC alignment layers [Figure 6(b)–(f)] and the homeotropic LC alignment was maintained for at least more than 12 months since we first made the LC cells from these polymers.

The pretilt angles of the antiparallel LC cells fabricated with the rubbed polymer films were measured in order to investigate the effect of the alkyl side groups on the LC alignment direction (Table 3 and Figure 7). At first, the pretilt angles of the LC molecules on the unrubbed/rubbed PS and PHP films with rubbing density < 50 could not be measured due to the random planar LC alignment. Pretilt angles of about 0° on the rubbed PS and PHP films were

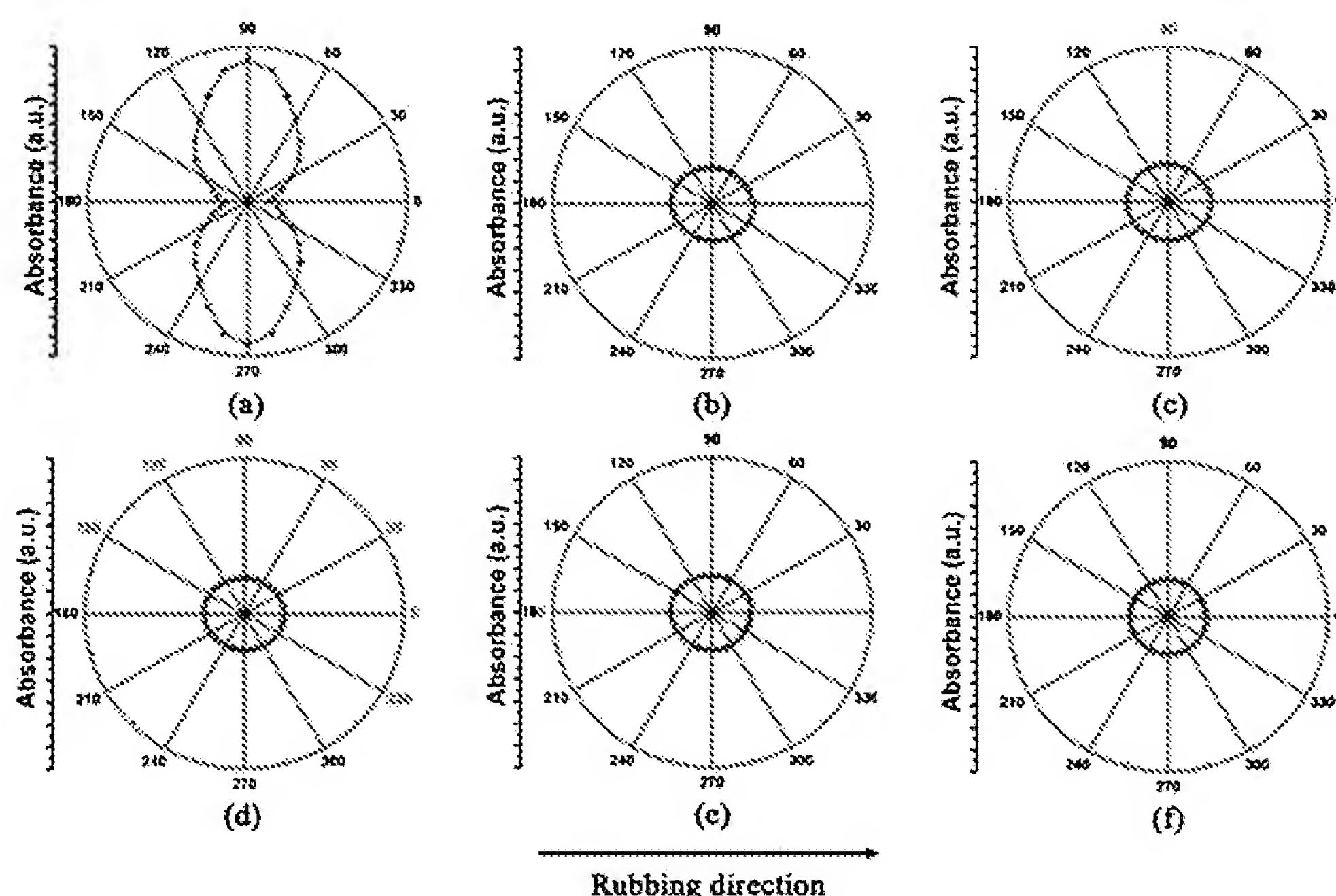


Figure 6. Polar diagrams of the absorbance of a dichroic dye (disperse blue 1) in antiparallel LC cells made from rubbed (a) PHP and 4-alkylphenoxyethyl-substituted polystyrenes [(b) P4MP, (c) P4EP, (d) P4BP, (e) P4HP, and (f) P4OP] films with a rubbing density of 100 as a function of rotation angle of samples.

Table 3. Surface energy values and LC alignment properties of the polymers.

Polymer designation	Contact angle ^{a)}		Surface energy ^{b)}			Homeotropic LC aligning ability	Pretilt angle ^{c)}		
	°		mJ · m ⁻²						
	Water	Methylene iodide	Dispersion	Polar	Total				
PS	82	28	42.37	3.17	45.54	No	0		
PHP	82	30	41.50	3.31	44.81	No	0		
P4MP	85	33	40.69	2.56	43.25	Yes	87.5		
P4EP	87	34	40.59	2.05	42.64	Yes	88.9		
P4EP78	86	33	40.88	2.27	43.15	Yes			
P4EP60	85	32	41.17	2.49	43.66	Yes			
P4EP37	84	26	43.60	2.41	46.02	No			
P4EP20	83	19	45.89	2.37	48.26	No			
P4BP	91	39	38.76	1.38	40.14	Yes	89.6		
P4HP	94	45	35.91	1.11	37.02	Yes	89.6		
P4OP	95	48	34.29	1.10	35.39	Yes	89.6		
4MP-PEO	77	34	38.67	5.64	44.31	No			
4OP-PEO	85	42	35.97	3.33	39.30	No			
8S-PS	86	62	24.21	5.65	29.85	No	0		
12S-PS	94	70	20.56	3.67	24.23	Yes	83.0		
16S-PS	97	72	19.79	2.92	22.71	Yes	85.0		
P3MP	83	28	42.57	2.84	45.41	No			
P2MP	83	25	43.57	2.98	46.57	No			

^{a)}Measured from static contact angles; ^{b)}calculated from Owens-Wendt's equation; ^{c)}measured from the antiparallel LC cells fabricated with rubbed polymer films with a rubbing density of 150.

obtained at rubbing density > 50. For example, the pretilt angles on the rubbed PS and PHP films with a rubbing density of 150 were found to be about 0°. On the contrary, the LC cells made from the unrubbed 4-alkylphenoxy-

methyl-substituted polystyrene films had pretilt angles of approximately 90° showing homeotropic LC alignment. The pretilt angles of the LC cells made from the rubbed films of 4-alkylphenoxy-methyl-substituted polystyrene with a rubbing density of 150 were observed in the range of 87.5–89.6°. The incorporation of a methyl group into the 4 position of PHP increases the pretilt angle to 87.5° and the pretilt angle increases slightly as the length of the alkyl group increases. The pretilt angles of the LC cells fabricated with the rubbed films of 4-alkylphenoxy-methyl-substituted polystyrenes were found to decrease as the rubbing density is increased from 0 to 250, as expected (Figure 7). For example, the pretilt angles of P4MP, P4EP, P4BP, P4HP, and P4OP decrease from 89.5 to 86.0°, 89.5 to 87.9°, 89.6 to 89.0°, 89.6 to 89.0°, and 89.9° to 88.9°, respectively. Therefore, the LC cells fabricated from the 4-alkylphenoxy-methyl-substituted polystyrenes maintain their high pretilt angles even at a very high rubbing density. The largest decrease of the pretilt angle of about 3.5° was observed from P4MP having the shortest alkyl groups among the 4-alkylphenoxy-methyl-substituted polystyrenes in this study. We tried to observe the differences of surface morphology of 4-alkylphenoxy-methyl-substituted

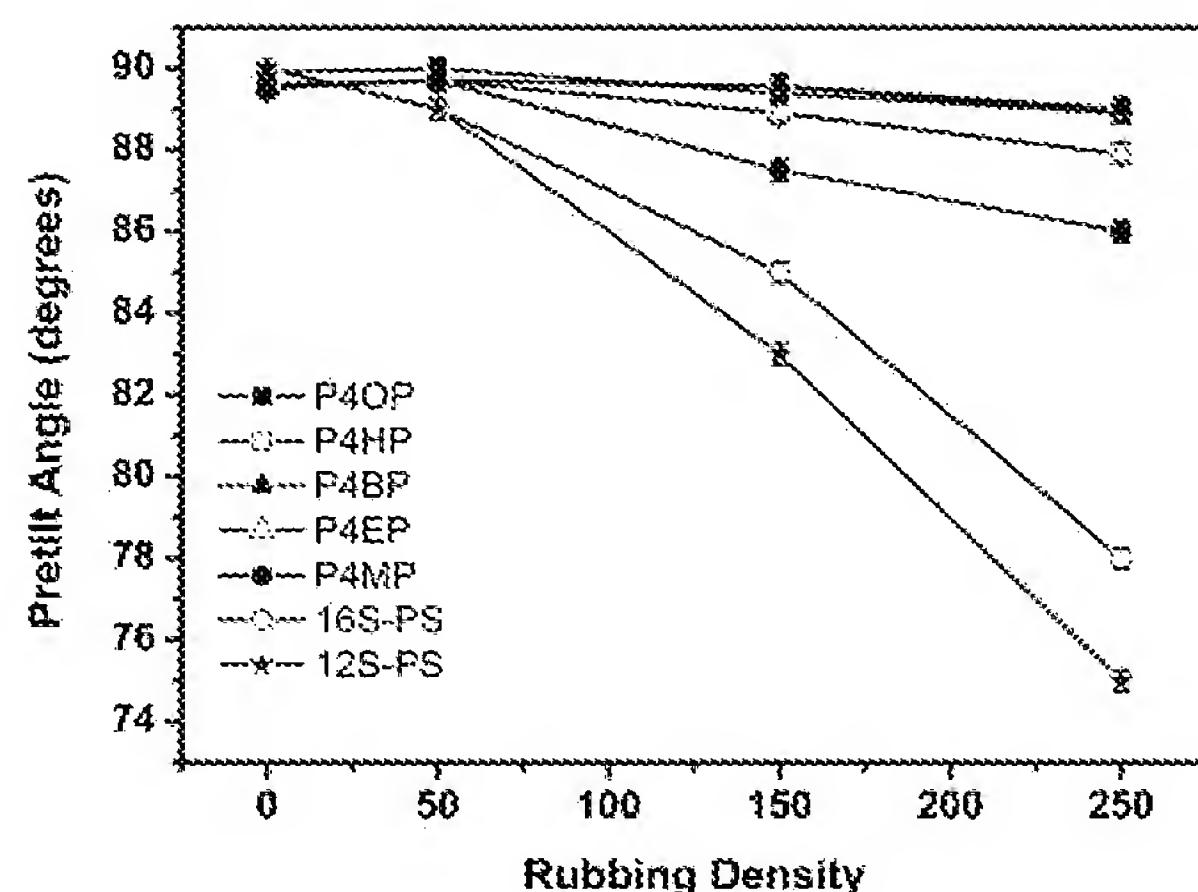


Figure 7. Pretilt angles of the antiparallel LC cells fabricated with rubbed films of 4-alkylphenoxy-methyl-substituted polystyrenes and *n*-alkylsulfonyl-methyl-substituted polystyrenes as a function of rubbing density.

polystyrenes having somewhat different homeotropic alignment behavior from AFM and TEM studies. While any morphological differences was not observed as shown in the Supporting Information.

The decrease of the pretilt angle of about 3.5° with increasing rubbing density of P4MP from 0 to 250 is much less than those of the other polystyrene derivatives showing homeotropic LC alignment behavior, such as the *n*-alkysulfonylmethyl-substituted polystyrenes (#S-PS).^[9] For example, the pretilt angles of the LC cells fabricated from the same LC (5CB) and the films of *n*-dodecylsulfonylmethyl-substituted polystyrene (12S-PS) and *n*-hexadecylsulfonylmethyl-substituted polystyrene (16S-PS) decrease from approximately 90° to 75 and 78° , respectively, when the rubbing density is increased from 0 to 250. Thus, in the case of 16S-PS having very long alkyl groups, the pretilt angle of the LCs changed from 90.0 to 78.0° when the rubbing density was increased from 0 to 250. The changes of the pretilt angles of the LCs on the films of the polystyrene derivatives are shown in Figure 7. We believe that the relatively small changes of pretilt angles of 4-alkylphenoxyethyl-substituted polystyrenes with the changes of rubbing density compared with those of other polystyrene derivatives should be arisen from their greater homeotropic LC aligning ability. The greater homeotropic LC aligning ability of the 4-alkylphenoxyethyl-substituted polystyrenes was further studied by comparing the alignment behavior of other polymers such as 4-methylphenoxyethyl-substituted poly(oxyethylene) (4MP-PEO), 4-octylphenoxyethyl-substituted poly(oxyethylene) (4OP-PEO), *n*-octylsulfonylmethyl-substituted polystyrene (8S-PS), 12S-PS, 16S-PS, 3-methylphenoxyethyl-substituted polystyrene (P3MP), and 2-methylphenoxyethyl-substituted polystyrene (P2MP) as shown in the next paragraph. The other polymers were prepared using a similar synthetic procedure to that used for the preparation of the 4-alkylphenoxyethyl-substituted polystyrenes and the detailed synthetic methods and ^1H NMR results are shown in the Supporting Information. 8S-PS, 12S-PS, and 16S-PS were synthesized using the same procedure as that described in a previous paper.^[9]

It has been known that LC cells fabricated from polymer surfaces having lower surface energy values show greater homeotropic LC aligning ability.^[9,16-18] We also found that the 4-alkylphenoxyethyl-substituted polystyrenes having longer side chains have a lower surface energy value and greater homeotropic LC aligning ability (Table 3). For example, the LC cell fabricated with P4OP having the lowest surface energy value among the 4-alkylphenoxyethyl-substituted polystyrenes maintains its high pretilt angle above 89° even at a very high rubbing density, while the pretilt angles of the LC cell made from P4MP having the highest surface energy value among the 4-alkylphenoxyethyl-substituted polystyrenes decreased

to 86.0° when a high rubbing density of 250 was used (Figure 7). However, we found that the surface energy value is not the critical factor determining the LC alignment behavior of the polystyrene derivatives and other polymers having similar structures. The POM images of the LC cells fabricated with other polymers, such as 4MP-PEO are shown in Figure 4. The surface energy values of 4OP-PEO and 8S-PS, 35.97 and $24.21 \text{ mJ} \cdot \text{m}^{-2}$, respectively, are much lower than those of the 4-alkylphenoxyethyl-substituted polystyrenes, while the LC cells fabricated from these polymers show poor LC alignment behavior. Therefore, we believe that not only the surface energy values of the polymers, but also the molecular orientation on the polymer surfaces, are important factors in obtaining homeotropic LC alignment behavior. Furthermore, random planar LC alignment behavior was observed from the LC cells fabricated from P3MP and P2MP. The chemical structures of P3MP and P2MP are almost identical to that of P4MP, except for the position of the methylphenoxy side groups. The surface energy values of P3MP and P2MP, 45.41 and $46.57 \text{ mJ} \cdot \text{m}^{-2}$, respectively, are slightly larger than that of P4MP. It has been reported that the LC alignment properties can be affected by the orientation of the isomeric functional side group in the polymer, due to the different steric repulsions or interactions between the LC molecules and the surfaces.^[19] Therefore, the different side chain orientation and/or the slightly larger surface energy of the P4MP and P3MP/P2MP polymers produce different LC alignment behavior.

Recently, there has been considerable effort aimed at developing plastic substrates for flexible LC displays.^[20] We found that the LC cells fabricated using the unrubbed films of 4-alkylphenoxyethyl-substituted polystyrenes on plastic (PET) substrates show good homeotropic LC alignment behavior. For example, the photo images of the unbent and bent LC cells made from P4EP on the PET substrate clearly show homeotropic LC alignment behavior (Figure 8). Furthermore, this LC cell showed very nice homeotropic LC aligning ability with a high pretilt angle of 90° , which was maintained for many times after bending. We also found that LC cells made from other 4-alkylphenoxyethyl-substituted polystyrenes such as

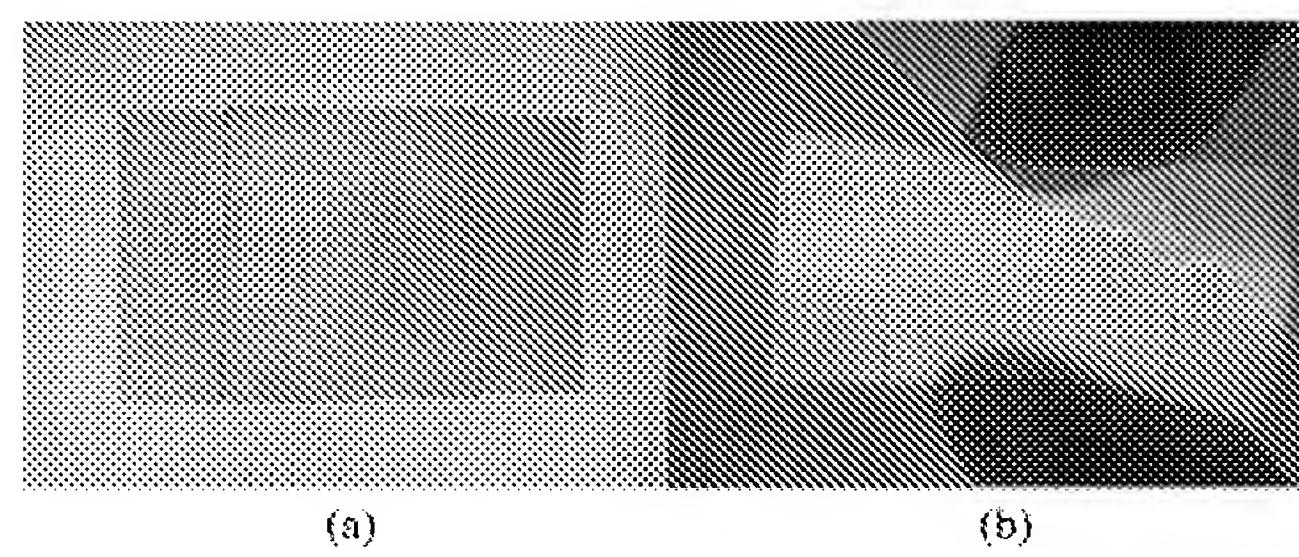


Figure 8. Photographs of the (a) unbent and (b) bent LC cells made from P4EP on the PET substrate.

P4MP, P4BP, P4HP, and P4OP on PET substrates also show the good homeotropic LC aligning ability. For example, POM images of LC cells made on PET substrates are shown in supporting information. Therefore, 4-alkylphenoxyethyl-substituted polystyrenes might be candidates as a LC alignment layer for flexible LC displays, such as for vertical alignment (VA) mode applications. Further research on the application of 4-alkylphenoxyethyl-substituted polystyrenes to flexible LC displays is currently in progress.

Conclusion

Phenoxyethyl-substituted polystyrene and 4-alkylphenoxyethyl-substituted polystyrenes were synthesized through the reactions of polychloromethylstyrene with phenol and 4-alkylphenols, respectively. The LC alignment direction on the mechanically rubbed surface of PHP was found to be homogeneous planar and perpendicular with respect to the rubbing direction. Interestingly, the LC cells made from the unrubbed and rubbed films of P4MP having only an additional methyl group in the 4 position of the phenoxy side groups showed homeotropic LC alignment behavior, while those prepared from the films of the P2MP and P3MP showed random planar LC alignment behavior. When we increased the number of carbons in the alkyl side groups in the 4-alkylphenoxyethyl-substituted polystyrenes, the homeotropic LC aligning ability increased; for example, a high pretilt angle of about 89.4° was observed from the LC cell prepared from the rubbed film of P4OP with a rubbing density of 150. On the contrary, the LC cells prepared from the unrubbed films of 4-octylphenoxyethyl-substituted polyoxyethylene and 4-octylsulfonylmethyl-substituted polystyrene showed planar LC alignment behavior. Therefore, the unique side chain structure, consisting of two phenyl groups and an alkyl group in the 4 position of the phenoxy groups of 4-alkylphenoxyethyl-substituted polystyrenes, imparts strong homeotropic LC alignment behavior. 4-Alkylphenoxyethyl-substituted polystyrenes could be a suitable candidate for the LC alignment layer in LCD modes, such as the VA mode for flexible LC display applications, because they have a high pretilt angle and low processing temperature.

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- [1] [1a] T. Kohki, H. Masaki, K. Mitsuhiro, I. Nobuyuki, H. Ray, S. Masanori, "Alignment Technologies and Applications of Liquid Crystal Devices", Taylor & Francis, New York 2005; [1b] K. Ichimura, *Chem. Rev.* 2000, **100**, 1847; [1c] M. O'Neill, S. M. Kelly, *J. Phys. D: Appl. Phys.* 2000, **33**, R67; [1d] P. Chaudhari, J. Lacey, J. Doyle, E. Galligan, S.-C. A. Lien, A. Callegari, G. Hougham, N. D. Lang, P. S. Andry, R. John, K.-H. Yang, M. Lu, C. Cai, J. Speidell, S. Purushothaman, J. Ritsko, M. Samant, J. Stohr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki, Y. Shiota, *Nature* 2001, **411**, 56; [1e] J.-H. Kim, M. Yoneya, H. Yokoyama, *Nature* 2002, **420**, 159; [1f] S. Varghese, S. Narayanan, C. W. M. Bastiaansen, G. P. Crawford, D. J. Broer, *Adv. Mater.* 2004, **16**, 1600; [1g] O. Yaroshchuk, Y. Zakrevskyy, S. Kumar, J. Kelly, L.-C. Chien, J. Lindau, *Phys. Rev. E* 2004, **69**, 011702; [1h] M. Gu, I. I. Smalyukh, O. D. Lavrentovich, *Appl. Phys. Lett.* 2006, **88**, 061110; [1i] Y. Yi, M. Nakata, A. R. Martin, N. A. Clark, *Appl. Phys. Lett.* 2007, **90**, 163510; [1j] H. Kang, K.-S. Kwon, D. Kang, J.-C. Lee, *Macromol. Chem. Phys.* 2007, **208**, 1853; [1k] J. B. Kim, C. J. Choi, J. S. Park, S. J. Jo, B. H. Hwang, M. K. Jo, D. Kang, S. J. Lee, Y. S. Kim, H. K. Baik, *Adv. Mater.* 2008, **20**, 3073; [1l] H. Kang, D. Kang, J.-C. Lee, *Polymer* 2009, **50**, 2104.
- [2] [2a] M. K. Ghosh, K. L. Mittal, "Polyimides: Fundamentals and Applications", Marcel Dekker, New York 1996; [2b] M. B. Feller, W. Chen, T. R. Shen, *Phys. Rev. A* 1991, **43**, 6778; [2c] N. A. J. van Aerle, J. W. Tol, *Macromolecules* 1994, **27**, 6520; [2d] K.-W. Lee, S.-H. Paek, A. Lien, C. Durning, H. Fukuro, *Macromolecules* 1996, **29**, 8894; [2e] J.-H. Kim, B. R. Acharya, S. Kumar, K. R. Ha, *Appl. Phys. Lett.* 1998, **73**, 3372; [2f] J. Stohr, M. G. Samant, A. Cossy-Favre, J. Diaz, Y. Momoi, S. Odahara, T. Nagata, *Macromolecules* 1998, **31**, 1942; [2g] R. Meister, B. Jerome, *Macromolecules* 1999, **32**, 480; [2h] J. J. Ge, C. Y. Li, G. Xue, I. K. Mann, D. Zhang, S.-Y. Wang, F. W. Harris, S. Z. D. Cheng, S.-C. Hong, X. Zhuang, Y. R. Shen, *J. Am. Chem. Soc.* 2001, **123**, 5768; [2i] D. Kim, M. Oh-e, Y. R. Shen, *Macromolecules* 2001, **34**, 9125; [2j] B. Chae, S. B. Kim, S. W. Lee, S. I. Kim, W. Choi, B. Lee, M. Ree, K. H. Lee, J. C. Jung, *Macromolecules* 2002, **35**, 10119; [2k] S. G. Hahn, T. J. Lee, T. Chang, J. C. Jung, W.-C. Zin, *Macromolecules* 2006, **39**, 5385; [2l] Y. J. Lee, J. G. Choi, I.-K. Song, J. M. Oh, M. H. Yi, *Polymer* 2006, **47**, 1555; [2m] K. E. Vaughn, M. Sousa, D. Kang, C. Rosenblatt, *Appl. Phys. Lett.* 2007, **90**, 194102.
- [3] [3a] T. Kagaiyo, K. Fujibayashi, T. Shimamura, H. Okada, H. Onnagawa, *Jpn. J. Appl. Phys.* 2005, **44**, 578; [3b] S.-C. Jeng, C.-W. Kuo, H.-L. Wang, C.-C. Liao, *Appl. Phys. Lett.* 2007, **91**, 061112; [3c] M. Talarico, A. Goleme, *Nat. Mater.* 2006, **5**, 185; [3d] H.-Y. Chen, W. Lee, N. A. Clark, *Appl. Phys. Lett.* 2007, **90**, 033510; [3e] K. A. Park, S. M. Lee, S. H. Lee, Y. H. Lee, *J. Phys. Chem. C* 2007, **111**, 1620.
- [4] [4a] S.-T. Wu, D.-K. Yang, "Reflective Liquid Crystal Displays", John Wiley & Sons, West Sussex 2001, Ch. 12; [4b] D.-K. Yang, S.-T. Wu, "Fundamentals of Liquid Crystal Devices", John Wiley & Sons, West Sussex 2001, Ch. 8.
- [5] S. W. Lee, S. I. Kim, Y. H. Park, M. Ree, Y. N. Rim, H. J. Yoon, H. C. Kim, Y.-B. Kim, *Mol. Cryst. Liq. Cryst.* 2000, **349**, 279.
- [6] Y. J. Lee, Y. W. Kim, J. D. Ha, J. M. Oh, M. H. Yi, *Polym. Adv. Technol.* 2007, **18**, 226.
- [7] S. W. Lee, B. Chae, B. Lee, W. Choi, S. B. Kim, S. I. Kim, *Chem. Mater.* 2003, **15**, 3105.

[8] S. B. Lee, G. J. Shin, J. H. Chi, W.-C. Zin, J. C. Jung, S. G. Hahm, M. Ree, T. Chang, *Polymer* **2005**, *47*, 6606.

[9] H. Kang, J. S. Park, D. Kang, J.-C. Lee, *Polym. Adv. Technol.* DOI: 10.1002/pat.1314.

[10] G. Odian, "Radical Chain Polymerization", in: *Principles of Polymerization*, 4th Edition, John Wiley & Sons, New York 2004, Ch. 3.

[11] D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* **1969**, *13*, 1741.

[12] G. I. Sprokel, "The Physics and Chemistry of Liquid Crystal Devices", 1st edition, Springer, New York 1980.

[13] [13a] B. Chae, S. B. Kim, S. W. Lee, S. I. Kim, W. Choi, B. Lee, M. Ree, K. H. Lee, J. C. Jung, *Macromolecules* **2002**, *35*, 10119; [13b] G. Socrates, "Infrared and Raman Characteristic Group Frequencies: Tables and Charts", 3rd Edition, John Wiley & Sons, New York 2004.

[14] [14a] R. A. Hayes, *J. Appl. Polym. Sci.* **1961**, *15*, 318; [14b] B. Wesslin, R. W. Lenz, W. J. MacKnight, F. E. Karaz, *Macromolecules* **1971**, *4*, 24; [14c] J.-C. Lee, M. H. Litt, C. E. Rogers, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 75.

[15] [15a] S. W. Lee, B. Chae, H. C. Kim, B. Lee, W. Choi, S. B. Kim, T. Chang, M. Ree, *Langmuir* **2003**, *19*, 8735; [15b] S. W. Lee, J. Yoon, H. C. Kim, B. Lee, T. Chang, M. Ree, *Macromolecules* **2003**, *36*, 9905; [15c] S. G. Hahm, T. J. Lee, S. W. Lee, J. Yoon, M. Ree, *Mater. Sci. Eng. B* **2006**, *132*, 54.

[16] H. Kang, J. S. Park, D. Kang, J.-C. Lee, *Macromol. Chem. Phys.* **2008**, *209*, 1900.

[17] [17a] B. S. Ban, Y. N. Rim, Y. B. Kim, *Liq. Cryst.* **2000**, *27*, 125; [17b] M. Lu, *Jpn. J. Appl. Phys.* **2004**, *43*, 8156; [17c] J.-B. Lee, H.-K. Lee, J.-C. Park, Y.-B. Kim, *Mol. Cryst. Liq. Cryst.* **2005**, *439*, 161.

[18] [18a] S.-K. Oh, M. Nakagawa, K. Ichimura, *J. Mater. Chem.* **2001**, *11*, 1563; [18b] Y. Matsuzawa, M. Matsumoto, *Mol. Cryst. Liq. Cryst.* **2004**, *412*, 181; [18c] H. J. Ahn, S. J. Rho, K. C. Kim, J. B. Kim, B. H. Hwang, C. J. Park, H. K. Baik, *Jpn. J. Appl. Phys.* **2005**, *44*, 4092; [18d] A. D. Price, D. K. Schwartz, *Langmuir* **2006**, *22*, 9753.

[19] [19a] K. Ichimura, *Chem. Rev.* **2000**, *100*, 1847; [19b] K. Ichimura, Y. Akita, H. Akiyama, K. Kudo, Y. Hayashi, *Macromolecules* **1997**, *30*, 903; [19c] S. I. Kim, M. Ree, T. J. Shin, J. C. Jung, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2909.

[20] B. A. MacDonald, K. Rollins, D. Mackerron, K. Rakos, R. Eveson, K. Hashimoto, B. Rustin, "Engineered Films for Display Technologies", in: *Flexible Flat Panel Displays*, G. P. Crawford, Ed., John Wiley & Sons, West Sussex 2005, Ch. 2.